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# Evaluating $\text{CaCO}_3$ -cycle modules in coupled global biogeochemical ocean models

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GMDD

6, 6117–6155, 2013

## Evaluating $\text{CaCO}_3$ -models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

The marine  $\text{CaCO}_3$  cycle is an important component of the oceanic carbon system and directly affects the cycling of natural and the uptake of anthropogenic carbon. In numerical models of the marine carbon cycle, the  $\text{CaCO}_3$  cycle component is often evaluated against the observed distribution of alkalinity. Alkalinity varies in response to the formation and remineralisation of  $\text{CaCO}_3$  and organic matter. However, it also has a large conservative component, which may strongly be affected by a deficient representation of ocean physics (circulation, evaporation, and precipitation) in models. Here we apply a global ocean biogeochemical model run into preindustrial steady state featuring a number of idealized tracers, explicitly capturing the model's  $\text{CaCO}_3$  dissolution, organic matter remineralisation, and various preformed properties (alkalinity, oxygen, phosphate). We compare the suitability of a variety of measures related to the  $\text{CaCO}_3$  cycle, including alkalinity (TA), potential alkalinity and  $\text{TA}^*$ , the latter being a measure of the time-integrated imprint of  $\text{CaCO}_3$  dissolution in the ocean. It can be diagnosed from any data set of TA, temperature, salinity, oxygen and phosphate. We demonstrate the sensitivity of total and potential alkalinity to the differences in model and ocean physics, which disqualifies them as accurate measures of biogeochemical processes. We show that an explicit treatment of preformed alkalinity ( $\text{TA}^0$ ) is necessary and possible. In our model simulations we implement explicit model tracers of  $\text{TA}^0$  and  $\text{TA}^*$ . We find that the difference between modeled true  $\text{TA}^*$  and diagnosed  $\text{TA}^*$  was below 10 % (25 %) in 73 % (81 %) of the ocean's volume. In the Pacific (and Indian) Oceans the RMS error of  $\text{TA}^*$  is below 3 (4)  $\text{mmol TA m}^{-3}$ , even when using a global rather than regional algorithms to estimate preformed alkalinity. Errors in the Atlantic Ocean are significantly larger and potential improvements of  $\text{TA}^0$  estimation are discussed. Applying the  $\text{TA}^*$  approach to the output of three state-of-the-art ocean carbon cycle models we demonstrate the advantage of explicitly taking preformed alkalinity into account for separating the effects of biogeochemical processes and circulation on the distribution

GMDD

6, 6117–6155, 2013

## Evaluating $\text{CaCO}_3$ -models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of alkalinity. In particular, we suggest to use the TA\* approach for CaCO<sub>3</sub>-cycle model evaluation.

## 1 Introduction

According to Sabine et al. (2004), the ocean has taken up about 43 % of the anthropogenic CO<sub>2</sub> emissions into the atmosphere since preindustrial times. The partitioning of CO<sub>2</sub> between atmosphere and the ocean is controlled by the buffer capacity of the CO<sub>2</sub>-system in the surface ocean together with the meridional overturning. The buffer capacity of the CO<sub>2</sub>-system varies with temperature and the distribution of total inorganic carbon and alkalinity (e.g. Omta et al., 2010, 2011). Biogeochemical processes, namely the organic tissue pump and the CaCO<sub>3</sub> counter pump, strongly affect the ocean's internal cycling and distribution of carbon and alkalinity, which in turn influences the surface ocean buffer capacity and hence the ocean's ability to take up anthropogenic CO<sub>2</sub>. Also, the invasion of CO<sub>2</sub> into the ocean leads to ocean acidification, which is suspected to modify life conditions in the surface ocean potentially changing fluxes of carbon and alkalinity within the ocean. Potential feedbacks are likely to exist on the ocean's future capacity to take up anthropogenic CO<sub>2</sub>. To better understand and quantify possible global implications of CO<sub>2</sub>-induced changes in ocean chemistry, numerical models of marine biogeochemistry and circulation are promising tools. Data-based model evaluation is an important step in the development of prognostic models suitable for studying the complex interactions of ocean acidification, global warming, ocean biogeochemistry, and their net effect on global ocean carbon uptake and storage.

Considerable effort has been devoted to the evaluation of models of the organic tissue pump, i.e. the production, transformations, and fluxes of organic matter in the ocean. The distributions of nutrients (e.g. phosphate), oxygen, as well as derived properties like AOU, the apparent oxygen utilization (Pytkowicz, 1971), provide suitable constraints on organic matter fluxes in the ocean (Najjar et al., 2007; Schneider et al.,

### Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2008; Kriest et al., 2010; Duteil et al., 2013). These tracers are suitable because the effects of ocean biology on them has a large signal-to-background ratio, i.e. the biotic effect is large compared with other effects. For example, the ratio of phosphate remineralised in the interior of the ocean to total observed phosphate ranges between 20 and 45 % in high latitudes and oxygen minimum zones, respectively. With AOU the signal-to-background ratio is even better. Were it not for uncertainties in the oxygen saturation assumption required in its computation (Duteil et al., 2013) the effect of biota on AOU would be almost 100 %. The skill of state-of-the-art models to represent the organic tissue pump may hence be well judged from their ability to reproduce the global distribution of AOU (Najjar et al., 2007) or the recently suggested Evaluated Oxygen Utilization (EOU, Duteil et al., 2013).

In contrast, evaluating models of the marine CaCO<sub>3</sub> cycle is more difficult. In this study we look for adequate tracers that are suited to evaluate the marine CaCO<sub>3</sub> cycle in biogeochemical models. Total alkalinity (TA) has frequently been used for this purpose. However, patterns of TA are not from the production and dissolution of CaCO<sub>3</sub> alone. In Sect. 2 we show that surface ocean patterns of TA are dominated by evaporation and precipitation. Using observations as well as model results we discuss these and other limitations of TA for model evaluation. In Sect. 3 we introduce an approach which has been proposed to explicitly account for non-CaCO<sub>3</sub> effects on TA, the TA\* concept (e.g. Feely et al., 2002). TA\* measures the time-integrated imprint of CaCO<sub>3</sub>-dissolution in the ocean. It is an analogue of AOU, which measures time-integrated oxygen utilization. In Sect. 4 we present our experimental approach to test the applicability of TA\* by means of model simulations, in which computed TA\* is compared with an explicit, idealized, TA\* model tracer. In Sect. 5 we present and discuss the results of this TA\* evaluation. Finally (Sect. 6), we apply the TA\* approach to real-ocean observations as well as several published models.

## 2 TA distribution and CaCO<sub>3</sub> transformations

Production and dissolution of CaCO<sub>3</sub> affect the concentrations of calcium, total dissolved inorganic carbon (TCO<sub>2</sub>), and total alkalinity (TA). However, it is only TA and TCO<sub>2</sub> for which the total number of observations and their distribution (GLODAP, Key et al., 2004) can support model evaluation on a global scale. The sensitivity of TCO<sub>2</sub> to production and dissolution of CaCO<sub>3</sub> is very low since TCO<sub>2</sub> is predominately modified by decay of organic matter and influenced by the invasion of anthropogenic CO<sub>2</sub>. In 99 % of the ocean interior, organic matter decay has a larger effect on TCO<sub>2</sub> than CaCO<sub>3</sub> dissolution (Fig. 1a). On the contrary, the effect of CaCO<sub>3</sub> dissolution on TA exceeds that of organic matter remineralisation in about 60 % of the ocean volume (Fig. 1b) making TA more appropriate to evaluate CaCO<sub>3</sub> models. Therefore TA is often used as a data constraint in global CaCO<sub>3</sub> modelling (e.g. Gehlen et al., 2007; Ilyina et al., 2009; Ridgwell et al., 2007).

A major concern, however, in using TA concentrations for data-based model evaluation is the fact that it has a large background. In the deep North Pacific Ocean, where the largest time-integrated imprint of CaCO<sub>3</sub> dissolution is observed (about 120 mmol TAM<sup>-3</sup>, Feely et al., 2002), it is equivalent to 5 % of the observed TA only. Everywhere else the contribution of CaCO<sub>3</sub> dissolution on TA is even lower. On a global average, the ratio of the CaCO<sub>3</sub>-dissolution imprint to TA-background is about 0.02. The global mean ratio of the alkalinity effect stemming from organic matter remineralisation to TA background is only 0.005. Contributions from N<sub>2</sub>-fixation, denitrification, sulfate reduction, and shelf alkalinity fluxes are even smaller or of local importance only. Due to the dominance of the TA background, TA behaves to a large extent like a conservative tracer, very much like salinity. In fact about 71 % of the variation of surface-ocean alkalinity of the GLODAP data composite is explained by salinity variation (Fig. 2). This is easily understood since alkalinity represents the charge balance of the major constituents of sea salt. Like salinity, surface ocean alkalinity is largely determined by evaporation and precipitation (e.g. Friis et al., 2003). In the ocean interior

GMDD

6, 6117–6155, 2013

### Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



its distribution is largely explained by advection and mixing of “preformed alkalinity” (Fig. 3a and b). In analogy to the concept of preformed nutrients or preformed oxygen (Redfield et al., 1963; Duteil et al., 2012, 2013) preformed alkalinity (in the following denoted  $TA^0$ ) refers to the alkalinity which a water mass had when last in contact with the atmosphere before being subducted (Chen and Millero, 1979). In the ocean interior  $TA^0$  is a strictly conservative tracer, whereas TA is variable due to transformations of CaCO<sub>3</sub> and organic matter. Although these principles apply both to models and the real ocean, there is the difficulty that in the real ocean  $TA^0$  cannot be separated from TA by measurements. In a model, the distribution of  $TA^0$  can be studied by designing an explicit tracer of  $TA^0$  (see Sect. 4 for details). Along a section at 30° W in the Atlantic (Fig. 4), the range of modelled  $TA^0$  values is equivalent to 97 % of the range of modelled TA, along a section at 150° W in the Pacific (not shown) the respective value is 69 % in our model (see Sect. 4 for a description of the model). Given that physical processes can never be represented perfectly in coupled biogeochemical circulation models (e.g. Doney et al., 2004), it is not recommendable to use the distribution of bulk TA as a descriptor of CaCO<sub>3</sub> transformations in a data-model comparison. Small deficiencies in the representation of  $TA^0$ , e.g. due to errors in the surface salinity balance, or errors in ocean circulation and mixing can have profound effect on TA distribution in the ocean interior. Apparently, good (Fig. 5a) or bad (Fig. 5c and d) fits of model and observed TA (Fig. 5b) may hence betray our judgement of the respective CaCO<sub>3</sub> modules.

Recognizing these shortcomings of using TA patterns to estimate CaCO<sub>3</sub> cycling, different approaches have been proposed to overcome them. For example, Howard et al. (2006), suggested a tracer  $Alk^* = Alk - Alk^{mean} / S^{mean} \cdot S$ , with  $Alk^{mean}$  and  $S^{mean}$  being the oceanwide means of alkalinity and salinity, respectively. Variation of this  $Alk^*$  tracer in the deep ocean is supposed to be driven by CaCO<sub>3</sub> dissolution (increase in alkalinity) and the remineralisation of organic matter (decrease in alkalinity) only (Howard et al., 2006). (For the purpose of not confusing Howard’s  $Alk^*$  tracer with other tracers we use in our study, we rewrite  $Alk^*$  as  $TA^{H06} = TA - TA_{ave} / S_{ave} \cdot S$ .) The emerging pattern of this tracer along a transect in the Atlantic (Fig. 6a) suggests a dominance of

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



CaCO<sub>3</sub> production (and/or organic matter remineralisation) in the North Atlantic and of CaCO<sub>3</sub> dissolution in waters originating from the Southern Ocean. Applying Howard's approach to our model tracer TA<sup>0</sup>, we compute the anomaly  $TA^0 - TA_{ave}^0 / S_{ave} \cdot S$ . As the TA<sup>0</sup> tracer behaves conservatively, its anomaly should not reflect any effects of either CaCO<sub>3</sub> dissolution or organic matter remineralisation. Ideally, the salinity-normalised TA<sup>0</sup>-anomaly should be constant everywhere. This is, however, not the case for the actual pattern in our model simulation (Fig. 6b). This pattern is very similar to the pattern of the Howard et al. (2006) tracer. The similarity between the simulated spurious patterns in Fig. 6b and those in Fig. 6a resembles the spurious behaviour of observed salinity-normalized TA in surface waters shown by Friis et al., 2003.

Another property suggested to obtain a tracer of CaCO<sub>3</sub> transformations, which excludes any effects of salinity and organic tissue production or remineralisation, is Potential Alkalinity (PALK = (TA + NO<sub>3</sub>)/S · 35, e.g. Sarmiento et al., 2002). Here, the salinity normalisation is to correct for the effects of the freshwater balance and the nitrate term is to compensate for the alkalinity effects of organic matter dynamics. Yet again, modelled patterns of both PALK and PALK<sup>0</sup> (= TA<sup>0</sup> + PO<sub>4</sub><sup>0</sup> · 16)/S · 35) in the Atlantic (Fig. 6c, d) trace characteristic water masses observed in the Atlantic Ocean, like North Atlantic Deep Water, Antarctic Intermediate Water and Antarctic Bottom Water. Also, PALK<sup>0</sup> should display a uniform distribution if salinity normalization were an effective means of cancelling out salinity effects since none of the ingredients of PALK<sup>0</sup> are subject to biogeochemical modifications.

In the real ocean, simple salinity normalization like in the TA<sup>H06</sup> or PALK metrics cannot remove water mass effects due to non-zero alkalinity freshwater sources (Robbins, 2001; Friis et al., 2003), which are highly variable on a global scale. In the Atlantic, for example, riverine zero-salinity alkalinity ranges from about 250 (Amazon) to 2500 (Mississippi) mmolm<sup>-3</sup> (e.g. Cai et al., 2010). Freshwater alkalinity depends on geochemical conditions of the respective drainage basins. In models alkalinity zero-salinity endmembers depend on model specific alkalinity ocean-boundary conditions. However, neither of these effects can explain the distribution of PALK and PALK<sup>0</sup> in the

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ocean's interior of our model simulation. Here, two additional problems of the PALK-concept become obvious: the biogenic modifications of TA in the surface ocean and the recirculation of TA, in particular in the Southern Ocean. CaCO<sub>3</sub> production in the surface ocean changes TA and consequently affects TA<sup>0</sup>. The PALK concept does not correct for this effect and hence the imprint of surface CaCO<sub>3</sub> production travels with PALK and PALK<sup>0</sup> through the interior of the ocean where, being subject to mixing, it complicates the interpretation of PALK with respect to CaCO<sub>3</sub> dissolution. Concerning the PALK (and TA<sup>H06</sup>) patterns in the South Atlantic, however, the recirculation of TA is likely to be most important. The Southern Ocean is the major site of deep water returning to the surface (Marshall and Speer, 2002). Water which has accumulated the imprint of CaCO<sub>3</sub> dissolution in the North Pacific returns to the surface in the Southern Ocean. Subsequently, most of this water is re-injected into the interior of the ocean either as Antarctic Intermediate Water or Antarctic Bottom Water. Similarly, the imprint of oxygen utilization in the ocean's interior wells up in the Southern Ocean, indicated by significant oxygen undersaturation there (Ito et al., 2004). Gas exchange with the atmosphere, however, is able to reset oxygen to values corresponding to surface temperature and salinity nearly completely. But for TA no equivalent restoring process to reset it to values consistent with actual surface salinity exists. The PALK pattern observed in the South Atlantic must hence be interpreted as a recirculation of the imprint of CaCO<sub>3</sub> dissolution which took place as far away as the North Pacific. We conclude that neither TA data nor derivatives like TA<sup>H06</sup> or PALK are well suited for the data-based evaluation of ocean CaCO<sub>3</sub>-cycle models.

In the next section we describe TA\*, a property suggested earlier as a measure of the time-integrated effect of CaCO<sub>3</sub> dissolution in the ocean (Feely et al., 2002; Sabine et al., 2002; Chung et al., 2003). The advantage of the TA\* approach is that it treats the issue of preformed alkalinity explicitly. We study the applicability of this method for the data-based evaluation of CaCO<sub>3</sub> cycle model components.



### 3 TA\* approach

The TA\* approach (Feely et al., 2002; Sabine et al., 2002; Chung et al., 2003) has been used to quantify the time-integrated imprint of CaCO<sub>3</sub> dissolution. Precursors of this method have been vital for the determination of anthropogenic CO<sub>2</sub> in the ocean since the early paper of Chen and Millero (1979). The underlying concept (Eq. 1) of the TA\* approach is that the observed alkalinity (TA) in the interior of the ocean is composed of a preformed component, TA<sup>0</sup>, a term due to the remineralisation of organic matter, TA<sup>r</sup>, and a term due to CaCO<sub>3</sub> dissolution, usually coined TA\*. (Unlike in other publications, and for the sake of direct comparison of computed TA\* and the TA\*-tracer introduced below, all terms are reported in units of mmol TA m<sup>-3</sup>).

$$TA = TA^0 + TA^* - TA^r \quad (1)$$

Remineralisation of organic matter, through the regeneration of nitrate, phosphate, and sulphate, decrement TA while the dissolution of CaCO<sub>3</sub> increments it (Wolf-Gladrow et al., 2007). The alkalinity effect of organic matter decomposition can be parameterized as a function of AOU, i.e.  $TA^r = r_{\text{Alk:NO}_3} \cdot r_{\text{NO}_3:-\text{O}_2} \cdot \text{AOU}$ . Values for  $r_{\text{NO}_3:-\text{O}_2}$  and  $r_{\text{Alk:NO}_3}$  are usually derived from observations, e.g.  $r_{\text{NO}_3:-\text{O}_2} = 1/10.625$ ,  $r_{\text{Alk:NO}_3} = 1.26$  (Anderson and Sarmiento, 1994; Kanamori and Ikegami, 1982), and are generally prescribed in biogeochemical models. Considering maximum values of AOU observed in the ocean (about 350 mmol O<sub>2</sub> m<sup>-3</sup>), the largest TA<sup>r</sup> is about 40 mmol TA m<sup>-3</sup>. The global average TA<sup>r</sup> (using AOU from World Ocean Atlas) is 18.1 mmol m<sup>-3</sup>. Considering that AOU overestimates true oxygen utilization by 20–25 % (Ito et al., 2004; Duteil et al., 2013), TA<sup>r</sup> computed from AOU is probably also overestimated by this percentage.

Preformed alkalinity denotes the alkalinity, which a water parcel had during its last contact with the atmosphere (Chen and Millero, 1979). Since all water masses in the interior of the ocean are mixtures of various end-members, the preformed alkalinity is also a mixture of different end-member alkalinity concentrations. For a given location

GMDD

6, 6117–6155, 2013

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in the ocean interior, neither the preformed alkalinity end-member concentrations nor their mixing ratios are known. Preformed alkalinity,  $TA^0$ , must therefore be diagnosed. This is usually done by an empirical approach which comprises two steps (e.g. Feely et al., 2002; Matsumoto and Gruber, 2007). First, a multi-linear regression of alkalinity with salinity, temperature and PO (or NO) is derived from near-surface data (Eq. 2).

$$TA^{\text{surf}} = a_0 + a_1 \cdot S^{\text{surf}} + a_2 \cdot T^{\text{surf}} + a_3 \cdot PO^{\text{surf}} \quad (2)$$

PO (or NO) are considered conservative tracers within the ocean (Broecker, 1974) and defined as  $PO = O_2 + r_{-O_2:PO_4} \cdot PO_4$ , and  $NO = O_2 + r_{-O_2:NO_3} \cdot NO_3$ , assuming that  $r_{-O_2:PO_4}$  and  $r_{-O_2:NO_3}$  are constant in the interior of the ocean ( $r_{-O_2:PO_4} = 170$ ;  $r_{-O_2:NO_3} = 10.625$ ; Anderson and Sarmiento, 1994). Second, the coefficients derived from surface data are subsequently applied to salinity, potential temperature and PO (or NO) data from the interior of the ocean to compute  $TA^0$  everywhere (Eq. 3):

$$TA^0(x, y, z) = a_0 + a_1 \cdot S(x, y, z) + a_2 \cdot \text{potT}(x, y, z) + a_3 \cdot PO(x, y, z) \quad (3)$$

We will here use salinity, temperature and PO from the upper 100 m to derive the regression coefficients of Eq. (2). Salinity normalization of alkalinity has been applied sometimes with the  $TA^*$  approach, but it is omitted here following Friis et al. (2003) and the results presented in Sect. 2. Given these estimates of  $TA^0$  and  $TA^r$  and observations or model tracer data of  $TA$ ,  $TA^*$  can be computed after rearranging Eq. (1).

## 4 Modelling approach

Though variants of the  $TA^*$  method have been in use for decades there has, to our knowledge, not been any explicit evaluation of this method. Here, we apply a prognostic global ocean carbon-cycle model for this purpose. The model consists of an offline representation of ocean physics providing transport and mixing within the ocean, a NPZD-type model to represent the organic tissue pump, and a  $CaCO_3$ -cycle module.

## Evaluating $CaCO_3$ -models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

For the physical model we use the transport matrix method (TMM) described in detail by Khatiwala et al. (2005) and Khatiwala (2007). In this approach, passive tracer transport is represented by a matrix operation involving the tracer field and a transport matrix, which has been extracted from the MIT general circulation model, a primitive equation ocean model (Marshall et al., 1997). Seasonally cycling (monthly) coarse resolution matrices were derived from a  $2.8^\circ \times 2.8^\circ$  global configuration of this model with 15 layers in the vertical, forced with monthly mean climatological fluxes of momentum, heat, and freshwater, and subject to a weak restoring of surface temperature and salinity to observations. The same transport matrices were employed by Kriest et al. (2012) in their data-based assessment of biogeochemical models.

The model of the organic tissue pump used with the TMM is the NPZD-O<sub>2</sub>-DOP model of Schmittner et al. (2005) as modified by Kriest et al. (2010, 2012). The primary model currency is phosphorus (phosphate, DOP, phytoplankton, zooplankton, detritus) with oxygen as an additional model tracer. The molar O<sub>2</sub> : P ratio is fixed at 170 (Anderson and Sarmiento, 1994). Sinking and remineralisation of detritus are parameterized by a combination of a constant remineralisation rate and particle sinking speeds increasing with depth, together reflecting a power law function of the flux profile (Martin et al., 1987) with an exponent of 1.075 (Kriest et al., 2010). The latter value has been found to yield global oxygen and phosphate distributions in good agreement with observations (Kriest et al., 2012).

In order to represent oceanic alkalinity in a pragmatic way we implement the tracer TA and couple the production and remineralisation of organic matter with fixed ratios to the uptake and release of phosphate in the NPZD-O<sub>2</sub>-DOP model. We use a TA : P ratio of 21.8. CaCO<sub>3</sub> is produced with a temperature-dependent inorganic carbon: organic carbon ratio bound to the rate of detritus production in the model. The global CaCO<sub>3</sub> export production of our model is  $0.9 \text{ GtCyr}^{-1}$ , similar to other models and observational estimates (Berelson et al., 2007). In our model, CaCO<sub>3</sub> export and dissolution are instantaneous and follow an exponential decay function with a decay length scale

of 2000 m. We present preindustrial Holocene steady-state results from a model run over 6000 yr of model integration.

#### 4.1 Idealized tracers

We implement a number of idealised tracers. The tracer of preformed alkalinity,  $TA^0$ , is restored to model TA everywhere at the surface and at every time step. In the interior of the model ocean this tracer has no sinks or sources, but is transported and mixed conservatively according to our model's physics. The  $TA^*$ -tracer is set to zero at the surface. In the interior of the model ocean this tracer collects the effect of  $CaCO_3$  dissolution whenever it occurs. Similarly, a  $TA^f$  tracer is set to zero at the surface and collects the alkalinity effect of organic matter remineralisation in the ocean interior. All idealised tracers are transported and mixed according to model physics. That is, in the model we perfectly know  $TA^0$ ,  $TA^*$ , and  $TA^f$  at any point and time. The model is run for 6000 yr until at basically each grid point of the model the sum of the idealised tracers equals the model's TA, i.e. Eq. (1) is fulfilled. In order to test the  $TA^*$  concept we shall compare the model tracers  $TA^0$  and  $TA^*$  (in the following denoted  $TA_{true}^0$  and  $TA_{true}^*$ ) with these two properties as diagnosed from the model TA,  $PO_4$ , T, S,  $O_2$ , and AOU, according to Eqs. (1)–(3). In the following the diagnosed properties are denoted  $TA_{diag}^0$  and  $TA_{diag}^*$ , respectively.

#### 4.2 $TA^0$ algorithms

The initial step in the  $TA^*$  approach is to derive a multi-linear relationship between alkalinity and temperature, salinity and PO in the surface ocean (see Eq. 2). Where  $TA^*$  has been computed from observations, such algorithms have been either based on global data sets (e.g. Matsumoto and Gruber, 2005) or basin-wide subsets (Feely et al., 2002; Sabine et al., 2002; Chung et al., 2003), depending on the scope of the respective studies. Here, we shall test whether a more regional algorithm will provide an improved estimate of  $TA^0$  and eventually  $TA^*$  for data from our model experiment.

### Evaluating $CaCO_3$ -models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





isolate the error related to the computation of  $TA^0$  we here ignore any error related to the estimation of  $TA^r$  from diagnosing AOU and use the explicit model tracer of  $TA^r$  when computing  $TA^*$ , i.e.  $TA_{diag}^* = TA - TA_{diag}^0 + TA_{true}^r$ .

Using a single global algorithm (Table 1, #1) derived from seasonally unbiased sampling of surface ocean data for the computation of preformed alkalinity, we can reproduce the  $TA_{true}^*$  distribution relatively well: The global average volume weighted RMS error of  $TA^*$  in the interior of the ocean (below 100 m) is  $5.8 \text{ mmol m}^{-3}$  (Table 2, #1) and the global mean profiles of  $TA_{diag}^*$  and  $TA_{true}^*$  show very similar vertical patterns with  $TA_{diag}^*$  being usually somewhat smaller than  $TA_{true}^*$  (Fig. 7a). The performance of the global algorithm varies with ocean basin, with RMS errors as low as  $2.8 \text{ mmol m}^{-3}$  and as high as  $10.4 \text{ mmol m}^{-3}$  in the Pacific and Atlantic Oceans, respectively (Table 2). Using  $TA^0$  algorithms derived from regional data reduces the RMS error slightly in the Atlantic and Indian Oceans, while increasing it in the Pacific Ocean. The surface alkalinity RMS error (column 1 in Table 2) has little predictive power for the RMS error of  $TA^*$  in the interior of the ocean. Basin-averaged vertical profiles (Fig. 7b–d), show excellent agreement of diagnosed and true  $TA^*$  in the Pacific while in the Atlantic  $TA_{diag}^*$  is an underestimate of  $TA_{true}^*$ . Basin-averaged vertical profiles of the  $TA^*$  RMS error (Fig. 8a) are rather uniform in the Pacific and Indian Ocean and has a subsurface maximum at 2000 m depth in the Atlantic Oceans. The basin-average relative error of  $TA^*$  is 10 % or less in the Pacific and Indian Oceans below about 1000 m water depth (Fig. 8c). In the Atlantic Ocean the relative error ( $TA_{RMS}^*/TA^* \times 100$ ) is higher throughout and above 30 % in most of the water column, because of large RMS errors and low  $TA^*$  signal strength (Fig. 8b).

Using seasonally biased surface data to derive the  $TA^0$  algorithms yields increased  $TA^*$  RMS errors for summer-biased sampling and usually slightly reduced  $TA^*$  RMS errors for winter-biased sampling (Table 3). However, the effects of seasonally biased surface sampling are modest. Again RMS errors of surface alkalinity have little predictive power for  $TA^*$  RMS errors. Using regional surface data to derive the  $TA^0$  algorithm

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



improves the TA\* computation in some cases, like in the Indian Ocean or in the Pacific Ocean during summer (Table 2). However, using only surface Atlantic Ocean data to derive the TA<sup>0</sup> algorithm does not solve the problem of high TA\* RMS errors there. It is worth noting that despite the large RMS errors, diagnosed TA<sup>0</sup> still resembles the overall regional patterns of true TA<sup>0</sup> in the interior of the Atlantic Ocean (Fig. 9). We speculate that this is caused by the complex mixture of waters subducted in the north and south with their different end-member properties. Neither the global nor the basin-scale TA<sup>0</sup> algorithm can predict TA<sup>0</sup> in the interior of the Atlantic Ocean well enough to enable reasonable TA\* estimates. This is also reflected by particularly large RMS errors of the TA<sup>0</sup> estimate in the North Atlantic Deep Water (NADW) (Fig. 9d), where the TA<sup>0</sup> algorithm overestimates TA<sup>0</sup> by 10–14 mmol m<sup>-3</sup> (Fig. 9c).

In Fig. 10 zonal averages of TA\*<sub>true</sub> in the Pacific and Atlantic Oceans are compared with the difference of diagnosed and true TA\* (Fig. 10). In intermediate waters of the Atlantic, but also in the North Atlantic Deep Water, uncertainties of TA\* are of similar magnitude as TA\*. It is only in Antarctic Bottom Water that uncertainties are small enough to detect TA\* in the Atlantic. In the Pacific the picture is quite different. TA\* is detectable almost everywhere except in surface and mode waters of the upper hundreds of meters.

As a note of caution it is stressed again that TA\* is a time-integrated property subject to advection and mixing. The occurrence of a large TA\* values does not indicate the rate of CaCO<sub>3</sub> dissolution to be particularly large there. This characteristic of TA\* is shared with many other cumulative properties, notably AOU, which represents the time-integrated measure of remineralisation of organic matter, not its actual, local rate. The observation of TA\* in shallow waters oversaturated with respect to the dominant minerals of CaCO<sub>3</sub>, calcite and aragonite, respectively, has sometimes been erroneously interpreted as indicating shallow CaCO<sub>3</sub> dissolution (see Friis et al., 2006, 2007 for a discussion). Here we show that, in addition, TA\* in these waters usually cannot be determined accurately due to uncertainties in the TA<sup>0</sup> estimate.

## 6 Application of the TA\* approach to GLODAP and three OCMIP5 models

Finally, we apply the TA\* approach to an observation-based data product and to the output from three different models available at the Ocean Carbon Cycle Model Inter-comparison Project data server (<http://ocmip5.ipsl.fr>; accessed April 2012). As for the observations, we combine the GLODAP gridded dataset of TA (Key et al., 2004) with  $T$ ,  $S$ ,  $\text{PO}_4$  and  $\text{O}_2$  from the annual climatology of the World Ocean Atlas 2009 (e.g. Antonov et al., 2009). As for the models, we use output prepared for the OCMIP5 control runs. Specifically, we use the first available annual time slice of either the CTL or HIST runs, representing the end of the respective model spin up. We use output of the IFM/UVIC2-8 (Oschlies et al., 2008; [http://ocmip5.ipsl.fr/models\\_description/ifm\\_uvic2-8.html](http://ocmip5.ipsl.fr/models_description/ifm_uvic2-8.html)), MPI-M-ESM (Ilyina et al., 2013; [http://ocmip5.ipsl.fr/models\\_description/mpi-m\\_cosmos.html](http://ocmip5.ipsl.fr/models_description/mpi-m_cosmos.html)) and IPSL/IPSL-CM4 (Aumont and Bopp, 2006; [http://ocmip5.ipsl.fr/models\\_description/ipsl\\_ipsl-cm4.html](http://ocmip5.ipsl.fr/models_description/ipsl_ipsl-cm4.html)) models. It is beyond the scope of this paper to provide a full evaluation or model intercomparison of the three models. Instead we focus on a comparison of global mean profiles of TA,  $\text{TA}^0$ ,  $\text{TA}^r$  and  $\text{TA}^*$  from the three models and the observations with the only objective to illustrate the advantage of explicitly accounting for preformed alkalinity in a data-based model evaluation.

The global mean profile of alkalinity in the observations is characterized by an absolute minimum at the surface, a shallow maximum at about 100 to 200 m, a subsurface minimum at about 500 m, and a broad maximum between 3000 m and the bottom (Fig. 11a). The three models reproduce this structure to different degrees. The UVIC2-8 tracks the overall vertical gradient well while not reproducing the small-scale subsurface structures. The MPI-ESM tracks the vertical structure well, albeit with a slightly too small overall vertical gradient, but has a clear negative offset of about  $80 \text{ mmol m}^{-3}$ . This offset is due to a rescaling of the global oceanic carbon content in order to compensate for losses to the sediment during the spinup. The IPSL-CM4 shows too high an alkalinity in the upper 1000 m and too low a TA in the deep ocean by up to  $40 \text{ mmol m}^{-3}$  each. Subdividing TA into its components ( $\text{TA}^0$ ,  $\text{TA}^*$ , and  $\text{TA}^r$ ) indicates that much of the

### Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





misfits or fits between the global mean profiles of the individual models and the data are due to differences in preformed alkalinity (Fig. 11b). This is the case for the negative offset of the MPI-ESM model, the wrong surface-to-deep gradient in IPSL-CM4, as well as the good agreement between UVIC2-8 and GLODAP concerning the surface-to-deep gradient and the overall shape of the vertical profiles. The subsurface shallow maxima and minima in the observed TA global profile are due to preformed TA<sup>0</sup> only, and they are not related to biogeochemical modifications of alkalinity. TA<sup>r</sup> (Fig. 11d) as diagnosed from AOU global mean profiles shows small differences between models and data, well in agreement with our expectations (see Sect. 5) that uncertainties in TA<sup>r</sup> contribute little to uncertainties in the computation of TA\*. The global mean profiles of TA\* (Fig. 11c) suggest more agreement between models (and data) as might have been guessed from the global mean profiles of TA (Fig. 11a) alone. Yet, the globally integrated TA\*-inventory of IPSL-CM4 and MPI-ESM is about 25 % smaller than in both the GLODAP and the UVIC2-8 model. Also the distribution of TA\* with respect to CaCO<sub>3</sub> saturation states varies considerably between models and observations (Table 4). In IPSL-CM4 and MPI-ESM, the models which underestimate global CaCO<sub>3</sub> dissolution, about two thirds of the integrated TA\* is found in waters where OmegaCA is less than 1, while much smaller fractions are observed in waters with higher saturation. In GLODAP data the former fraction is about 55 % while the UVic model has only 43 % of integrated TA\* in undersaturated water. A large fraction of TA\* in undersaturated water is in agreement with expectations from dissolution chemistry. Overall, differences between observations and models both in the global integral of TA\* and its distribution point to larger uncertainties in the CaCO<sub>3</sub> modules of coupled carbon cycle models compared with the representation of the organic tissue pump: on a global scale the time-accumulated imprint of organic matter remineralisation on the oxygen distribution as measured by AOU of several state of the art models agreed within ± 10 % with observed AOU (Duteil et al., 2013; see also Fig. 11d).

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## 7 Conclusions

In this study we tested the applicability of the TA\* approach (Feely et al., 2002) in order to quantify the time-integrated and advected signal of CaCO<sub>3</sub> dissolution in models and observations by means of an ocean carbon cycle model augmented with idealized tracers of CaCO<sub>3</sub> dissolution. The method of computing TA\* according to the scheme described in Sect. 3 is found to reproduce tracer-based TA\* in our model experiment robustly in most of the global ocean. It is mainly in the Atlantic Ocean, but also in the upper 500 to 1000 m of the Pacific and Indian Oceans, respectively, where computed TA\* has elevated uncertainty, which make it unsuited to derive cumulative CaCO<sub>3</sub> dissolution in these waters. Since most of this uncertainty arises from the uncertainty of the TA<sup>0</sup> estimate, alternative approaches to derive isopycnal-specific preformed alkalinity, e.g. from methods of isopycnal analysis (e.g. Körtzinger et al., 2001), in combination with techniques to estimate water mass fractions in the ocean interior (e.g. Karstensen and Tomczak, 1998; Khatiwala et al., 2012) may be worth testing for regional applications.

As demonstrated from observations and model experiments, TA includes a large (and generally dominant) fraction of preformed alkalinity, closely associated with the salinity field and hence the physics of the ocean. Approaches in which alkalinity is normalized to salinity, like PALK or TA<sup>H06</sup> are, however, shown to produce artificial patterns in the interior of the ocean often unrelated to local biogeochemical processes. These TA derivatives do not fully remove the salinity association of patterns. In addition TA derivatives can be biased by the imprint of remote biogeochemical processes. For example, Southern Ocean upwelling and re-injection of water with an imprint from CaCO<sub>3</sub> dissolution in the North Pacific can give the false impression of CaCO<sub>3</sub> dissolution taking place in the South Atlantic. We conclude that data-model comparisons based on TA or salinity-normalised alkalinity alone cannot evaluate the CaCO<sub>3</sub> model independently of any possible deficiencies in the physical model.

GMDD

6, 6117–6155, 2013

### Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In the TA\* approach the conservative component of alkalinity is treated explicitly and separated from the biogeochemical effect, a procedure which turned out to be successful in much of the ocean in our method-evaluation model experiment. Applying the TA\* approach to model output from three state-of-the-art ocean carbon-cycle models we demonstrated the advantage of explicitly taking preformed alkalinity into account when comparing a range of CaCO<sub>3</sub> cycle models with observations. The comparison of this though limited number of models with observations points to larger uncertainties in CaCO<sub>3</sub>-modules of coupled carbon cycle models compared with the representation of the organic tissue pump in these models.

Finally, we propose to use the TA\* approach for the data-based evaluation of models of the oceanic CaCO<sub>3</sub>-cycle. Similar to a proposal made for the organic tissue pump by Najjar et al. (2007), we suggest to implement idealized tracers of either TA<sup>0</sup> or TA\* in ocean biogeochemical models in order to ease model intercomparison, but also to decide whether the results from this model study are applicable to a wider range of ocean models.

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## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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- 10

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## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



Evaluating  
CaCO<sub>3</sub>-models of the  
ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table 1.** TA<sup>0</sup>-algorithms. Algorithms are derived from surface data (upper 100 m) of the model. Subsets “winter data” “summer data”) use surface data from winter (summer) months of the respective hemispheres only. Basin-specific algorithms are based on data from the respective ocean basin.

#	Subset	Equation
Global		
1	all months	$TA^0 = 370.5765 + 54.0812 \cdot S + 0.3804 \cdot T + 0.1129 \cdot PO$
2	winter data	$TA^0 = 357.9100 + 54.3812 \cdot S + 0.3824 \cdot T + 0.1130 \cdot PO$
3	summer data	$TA^0 = 336.2851 + 55.0656 \cdot S + 0.4047 \cdot T + 0.1167 \cdot PO$
Atlantic		
4	all months	$TA^0 = 263.3001 + 56.1655 \cdot S + 1.4997 \cdot T + 0.1702 \cdot PO$
5	winter data	$TA^0 = 122.0885 + 59.9151 \cdot S + 1.5293 \cdot T + 0.1857 \cdot PO$
6	summer data	$TA^0 = 323.8251 + 54.4048 \cdot S + 1.6823 \cdot T + 0.1737 \cdot PO$
Pacific		
7	all months	$TA^0 = 559.3595 + 49.0273 \cdot S + 0.0923 \cdot T + 0.0861 \cdot PO$
8	winter data	$TA^0 = 550.7772 + 49.3419 \cdot S - 0.0299 \cdot T + 0.0794 \cdot PO$
9	summer data	$TA^0 = 506.9215 + 50.5235 \cdot S + 0.1332 \cdot T + 0.0903 \cdot PO$
Indic		
10	all months	$TA^0 = 844.9869 + 40.6930 \cdot S + 0.0261 \cdot T + 0.0960 \cdot PO$
11	winter data	$TA^0 = 715.8663 + 44.1346 \cdot S + 0.2181 \cdot T + 0.1095 \cdot PO$
12	summer data	$TA^0 = 824.6536 + 41.4498 \cdot S - 0.1242 \cdot T + 0.0902 \cdot PO$

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table 2.** Volume weighted root mean square (RMS) errors of global and regional TA<sup>0</sup> and TA\* estimates. Errors given in column “Surface” refer to the ability of the respective algorithm to reproduce the surface (upper 100 m) alkalinity of the model. Under TA<sup>0</sup> RMS errors of subsurface preformed TA as compared with TA<sup>0</sup> from the explicit tracer are given. Under TA\* RMS errors of computed TA\* compared with TA\* from the explicit tracer are given. Global algorithms are also evaluated concerning their skill on regional scales.

Algorithm	Surface	Global		Atlantic		Pacific		Indic	
		TA <sup>0</sup>	TA*	TA <sup>0</sup>	TA*	TA <sup>0</sup>	TA*	TA <sup>0</sup>	TA*
Global	9.6	6.5	5.9	10.2	10.4	4.3	2.8	4.4	3.8
Atlantic	9.7			10.3	10.1				
Pacific	9.2					3.1	3.5		
Indic	5.9							3.2	2.7

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table 3.** Volume weighted RMS errors for TA<sup>0</sup> and TA\* estimates based on seasonally unbiased TA<sup>0</sup> algorithm (all months) and winter and summer biased algorithms respectively. Column “surface” refers to the skill of the respective algorithm to reproduce the surface (upper 100 m) alkalinity of the model. Column TA<sup>0</sup> gives RMS errors of subsurface preformed TA as compared with TA<sup>0</sup> from the explicit tracer. Column TA\* gives the RMS of computed TA\* compared with TA\* from the explicit tracer. Global algorithms are also evaluated concerning their skills on regional scales.

Algorithm	Surface	Global		Atlantic		Pacific		Indic	
		TA <sup>0</sup>	TA*	TA <sup>0</sup>	TA*	TA <sup>0</sup>	TA*	TA <sup>0</sup>	TA*
Global									
all months	9.6	6.5	5.9	10.2	10.4	4.3	2.8	4.4	3.8
winter data	9.7	5.2	5.2	9.0	9.0	2.8	3.0	2.6	2.3
summer data	9.3	8.2	7.3	12.3	12.2	6.0	3.9	6.4	5.7
Atlantic									
all months	9.8			10.3	10.1				
winter data	9.7			9.3	9.2				
summer data	9.3			11.2	11.1				
Pacific									
all months	9.2					3.1	3.5		
winter data	9.2					3.0	4.6		
summer data	9.0					4.1	3.0		
Indic									
all months	5.9							3.2	2.7
winter data	6.2							2.2	2.0
summer data	5.4							5.1	4.4

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

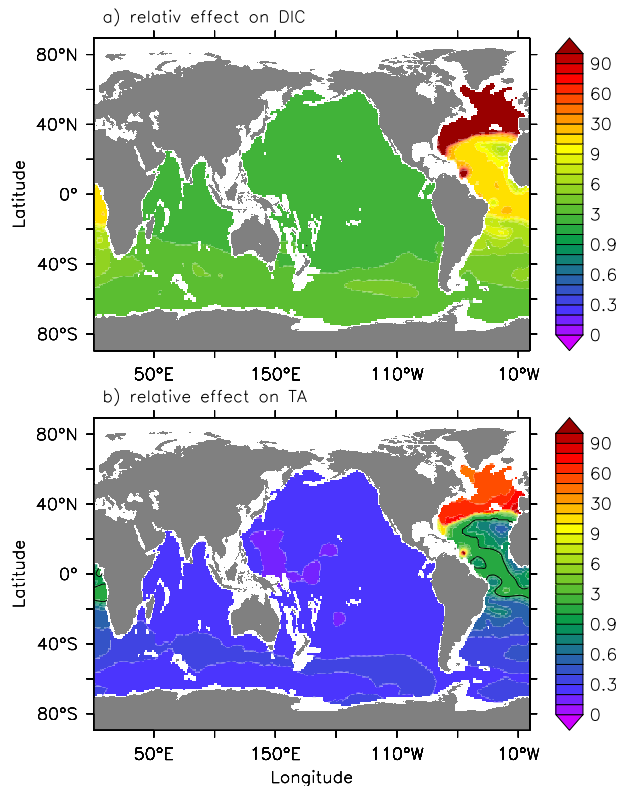
Interactive Discussion



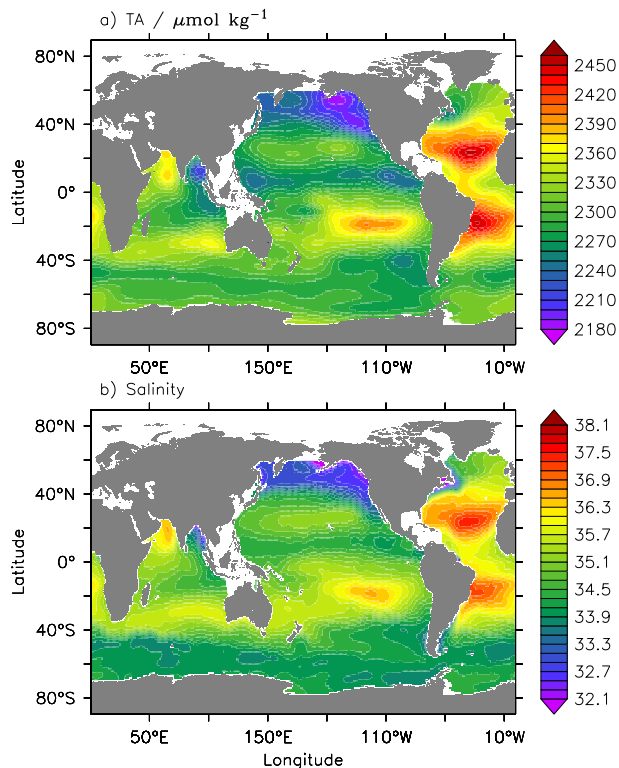
**Table 4.** Global TA\* inventories and its fractions with respect to the CaCO<sub>3</sub> saturation states.

Model	Global TA* inventory P molC	OmegaCa < 1 %	OmegaCa ≥ 1 and OmegaAR < 1 %	OmegaAR ≥ 1 %
GLODAP	38.9	55.3	41.3	3.4
IFM-UVIC28	40.0	43.0	49.1	7.9
IPSL-CM4	29.3	71.7	13.7	14.6
MPI-ESM	28.7	67.8	21.7	10.5

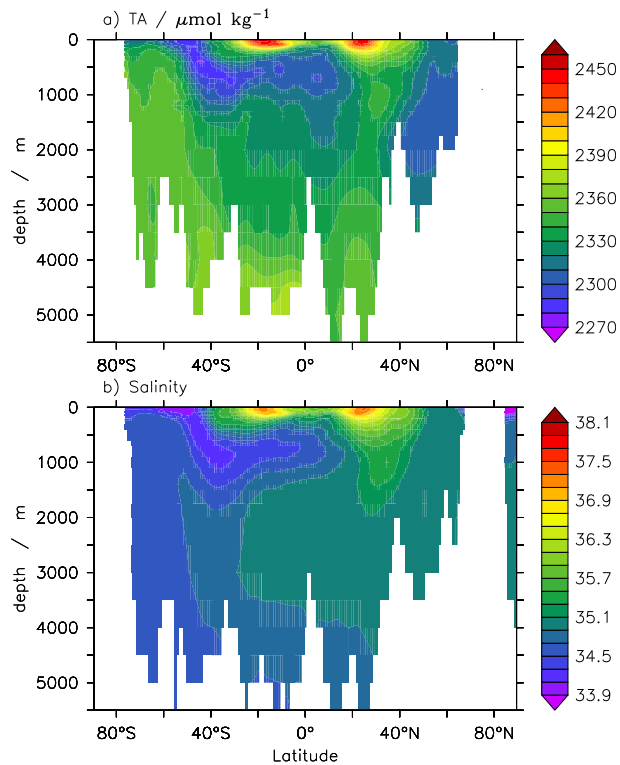
GLODAP is not defined north of 65° N. Model inventories and fractions are computed using the ocean volumes of the given model and the omega distribution in the respective models.



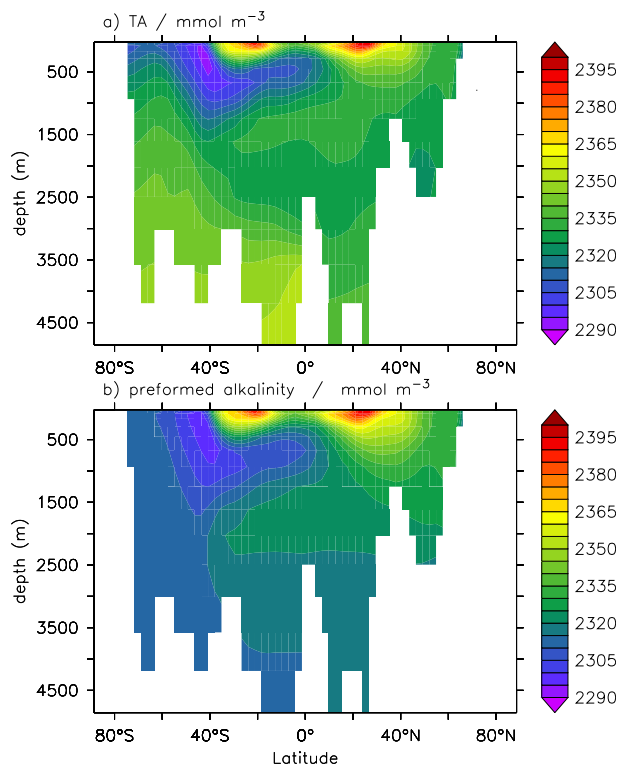
**Fig. 1.** Ratio of the imprint of the organic tissue pump and the  $\text{CaCO}_3$  pump on  $\text{TCO}_2$  **(a)** and TA **(b)** at 2000 m water depth.  $\Delta\text{DIC}^{\text{tissue}}$  and  $\Delta\text{TA}^{\text{tissue}}$  are computed from estimates of the apparent oxygen utilization (AOU) and the mean molar oxygen:carbon ratio of 1.4 and the mean molar oxygen:alkalinity ratio of 0.119 ( $= 1/170 \cdot 16 \cdot 1.26$ ), respectively. AOU is estimated using oxygen, potential temperature and salinity data from the World Ocean Atlas (gridded data, analysed annual means).  $\Delta\text{TA}^{\text{CaCO}_3}$  is computed using the  $\text{TA}^*$  method described in Sect. 3 applied to the GLODAP gridded dataset (Key et al., 2004).  $\Delta\text{DIC}^{\text{CaCO}_3} = 2 \times \text{TA}^*$ .



**Fig. 2.** Surface ocean distribution of TA (**a**, GLODAP, gridded data, [http://cdiac.ornl.gov/ftp/oceans/GLODAP\\_Gridded\\_Data/](http://cdiac.ornl.gov/ftp/oceans/GLODAP_Gridded_Data/), last access: 10 December 2009) and salinity (**b**, World Ocean Atlas, WOA, analysed annual means, Antonov et al., 2010). The scaling of the iso-lines was chosen to emphasize the global linear relationship between alkalinity ( $\mu\text{mol kg}^{-1}$ ) and salinity. With ungridded bottle data from the upper 100 m of the ocean (GLODAP/WAVES dataset, <http://cdiac3.ornl.gov/waves/discrete/>, last access: 31 March 2012) this relationship is  $\text{TA} = 699.75 + 46.18 \cdot S$ ;  $r^2 = 0.71$ .



**Fig. 3.** Horizontal sections of alkalinity (**a**, GLODAP) and salinity (**b**, WOA) along 30°W in the Atlantic Ocean. For the scaling of the isolines see caption of Fig. 2. Alkalinity patterns, particularly in the upper 2000 m, largely follow patterns of salinity indicating a predominantly conservative behaviour of alkalinity in the interior of the Atlantic Ocean.



**Fig. 4.** Distribution of total alkalinity **(a)** and a preformed alkalinity tracer **(b)** along 30° W from a model run (TMM-MIT28, see Sect. 4 for details of the model experiments). The preformed alkalinity ( $TA^0$ ) tracer is restored at the surface and at any time step of the model run to total alkalinity. In the interior of the model ocean  $TA^0$  has no biogeochemical sources or sinks but is advected and mixed conservatively. TA in this model is affected by both physical and biogeochemical processes.



Evaluating  
CaCO<sub>3</sub>-models of the  
ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

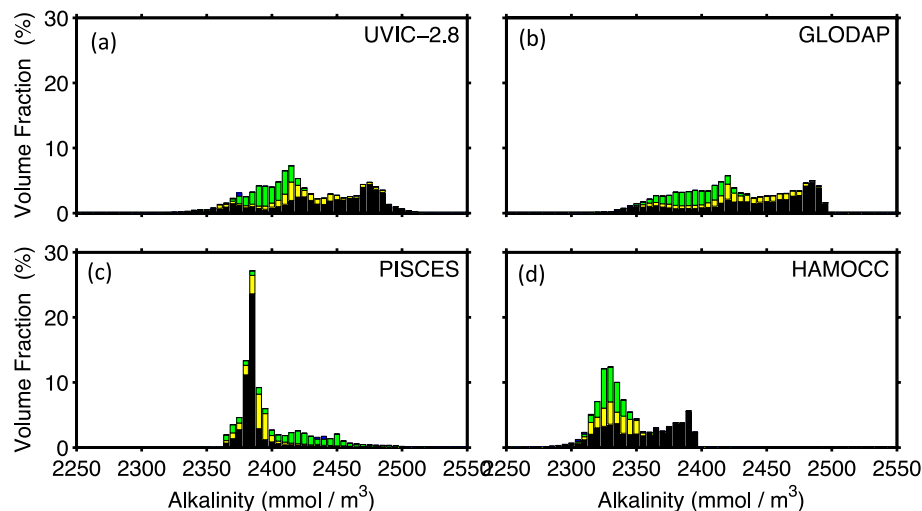
Back

Close

Full Screen / Esc

Printer-friendly Version

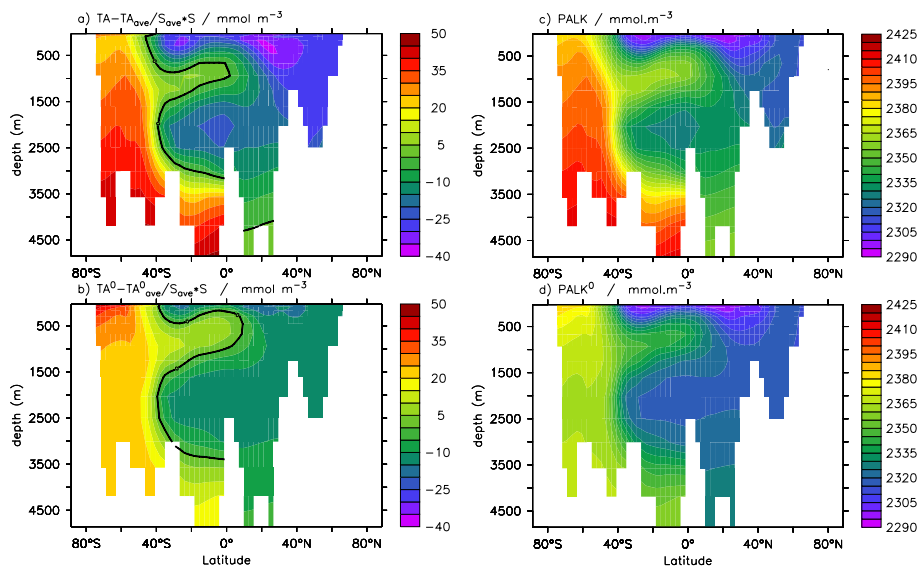
Interactive Discussion



**Fig. 5.** Global ocean volume-weighted frequency-distribution of alkalinity in observations (GLODAP dataset, Key et al., 2004) and three global carbon cycle models (see Duteil et al., 2012 for details). Fractions of the Atlantic, Pacific, Indian and Arctic Oceans are indicated by colour codes (green, black, yellow and blue, respectively).

Evaluating  
CaCO<sub>3</sub>-models of the  
ocean

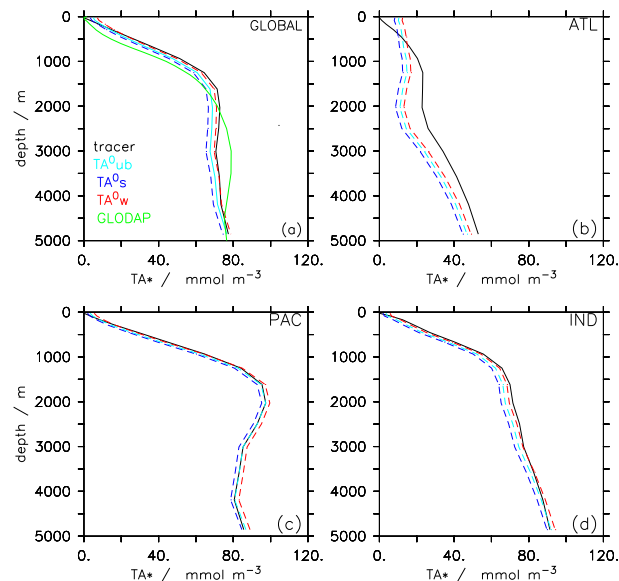
W. Koeve et al.



**Fig. 6.** Anomalies of TA **(a)** and a TA<sup>0</sup> **(b)** and the respective salinity normalised properties. **(c)** Potential alkalinity ( $PALK = (ALK + PO_4 \cdot 16) / S \cdot 35$ ) distribution along a section through the Atlantic. **(d)** Potential preformed alkalinity ( $PALK^0 = (TA^0 + PO_4^0) / S \cdot 35$ ). The distribution along 30° W from a model run (TMM-MIT28, see Sect. 4 for details of the model experiments) is shown.

## Evaluating CaCO<sub>3</sub>-models of the ocean

W. Koeve et al.

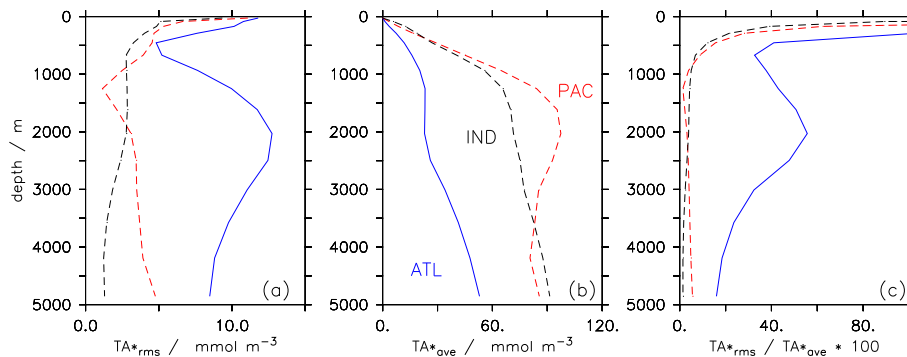


**Fig. 7.** (a) Global mean profile of  $TA^*$  from explicit model tracer (black, solid) and computed from model data (dashed). The two dashed lines are based on seasonally biased sampling of the model output at the surface when deriving the  $TA^0$  algorithm.  $TA_s^0$  refers to sampling during summer,  $TA_w^0$  refers to winter sampling when deep water actually forms. (Final version of the figure will include a third dashed line (lying between the two) which is based on unbiased sampling.) For comparison, the green line shows the global mean profile of  $TA^*$  computed from the GLODAP database and using a globally uniform algorithm derived from the gridded surface GLODAP data. (b–d). Basin-averaged profiles of  $TA^*$  for the Atlantic, Pacific and Indian Oceans. Tracer based estimate (black, solid) and computed  $TA^*$  from winter and summer biased  $TA^0$  algorithms are shown.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Evaluating  
CaCO<sub>3</sub>-models of the  
ocean

W. Koeve et al.



**Fig. 8.** Basin-average vertical profiles of TA\* RMS error (a), TA\* (b) and the percent ratio of the two (c). Blue solid: Atlantic Ocean. Red dashed: Pacific Ocean. Black dashed: Indian Ocean.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Evaluating  
CaCO<sub>3</sub>-models of the  
ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

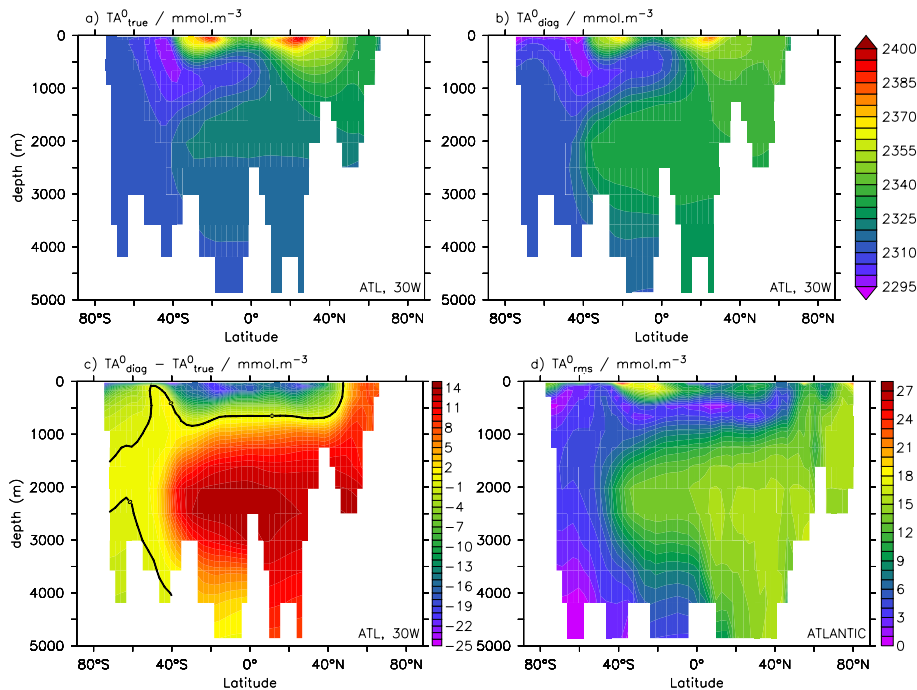
Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Fig. 9.** TA<sup>0</sup> distribution in the Atlantic Ocean from explicit tracer (a) and computed from winter biased surface sampling (b). Panel (c) shows the anomaly between the two and panel (d) the basin average RMS error of TA<sup>0</sup>.

Evaluating  
CaCO<sub>3</sub>-models of the  
ocean

W. Koeve et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

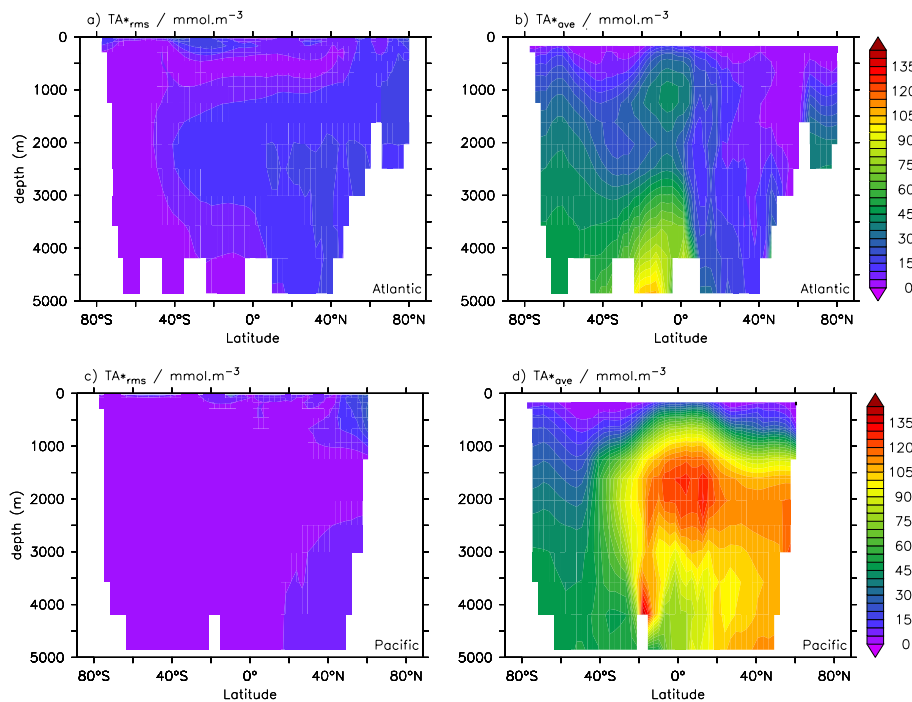
Back

Close

Full Screen / Esc

Printer-friendly Version

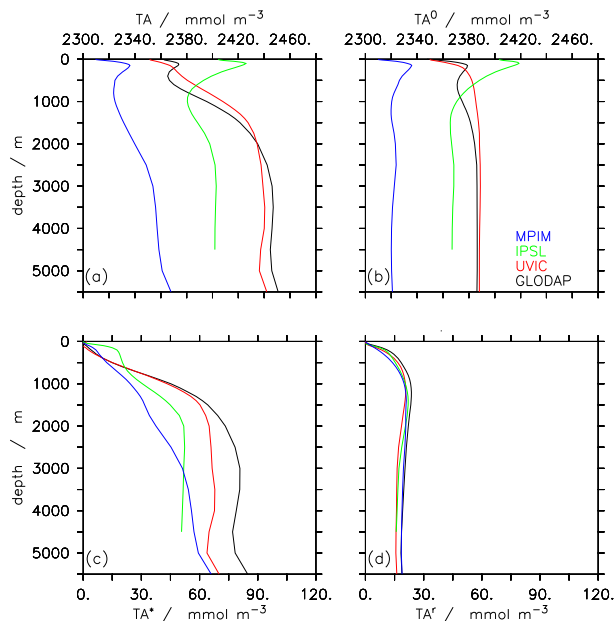
Interactive Discussion



**Fig. 10.** Basin averages of tracer-based  $TA^*$  (**b, d**) and its RMS error (computed  $TA^*$  vs. tracer  $TA^*$ ) from the Atlantic Ocean (**a**) and the Pacific Ocean (**c**).

Evaluating  
CaCO<sub>3</sub>-models of the  
ocean

W. Koeve et al.



**Fig. 11.** Global mean profiles of TA **(a)**, TA<sup>0</sup> **(b)**, TA\* **(c)**, and TA<sup>r</sup> **(d)** in the GLODAP dataset and in three different models. Properties in **(b–d)** are diagnosed according to the methods described in Sect. 3. For each of the datasets a specific TA<sup>0</sup>-algorithm was derived from annual mean data (models) or the annual composite GLODAP data, respectively (see text for details and insert for colour code of the models and data used).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

